

OXIDATION AND CHEMILUMINESCENCE OF TETRAKIS(DIMETHYLAMINO)ETHYLENE.

I. REVERSIBLE REACTIONS OF OXYGEN WITH TETRAKIS- (DIMETHYLAMINO)ETHYLENE AND *n*-DECANE

by

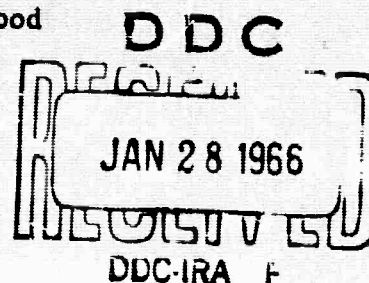
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ABSTRACT. The solubility and heat of solution of oxygen in *n*-decane and tetrakis(dimethylamino)-ethylene (TMAE) have been measured and found to be almost equal. The spectrally measurable interaction species, TMAE-O₂ and *n*-C₁₀H₂₂-O₂, are shown to have very low ΔH of formation (-1.2 and -0.4 kcal.). Thus, in nonpolar media the good electron donor TMAE and poor electron donor *n*-decane react similarly with oxygen.



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U. S. NAVAL ORDNANCE TEST STATION

China Lake, California

December 1965

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FOREWORD

This report covers a portion of the work performed at this Station on the compound tetrakis(dimethylamino)ethylene (TMAE). A particularly interesting feature of TMAE is the chemiluminescence which occurs during the course of its reaction with molecular oxygen. To investigate the mechanism of the autoxidation and chemiluminescence of TMAE, it was of importance to study any interactions between TMAE and oxygen. It is shown in this report that TMAE reversibly forms a donor-acceptor complex with oxygen and that the enthalpy change for this reaction is quite similar to the change for the reaction of oxygen and the poor electron-donor *n*-decane.

This work was initiated in 1963 under the sponsorship of the Chemistry Office of the Advanced Research Projects Agency through ARPA Order No. 285-62 AM5. Support was continued under Bureau of Naval Weapons Task Assignment RMMO 32-024/216-1/F008-17-02, Problem Assignment No. 4. The work was completed in the early part of 1965.

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Oxidation and Chemiluminescence of Tetrakis(dimethylamino)ethylene. I.

Reversible Reactions of Oxygen with Tetrakis(dimethylamino)ethylene and *n*-Decane

by Carl A. Heller and Aaron N. Fletcher

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The solubility and heat of solution of oxygen in *n*-decane and tetrakis(dimethylamino)ethylene (TMAE) have been measured and found to be almost equal. The spectrally measurable interaction species, TMAE-O₂ and *n*-C₁₀H₂₂-O₂, are shown to have very low ΔH of formation (-1.2 and -0.4 kcal.). Thus, in nonpolar media the good electron donor TMAE and poor electron donor *n*-decane react similarly with oxygen.

Introduction

This paper will describe studies of a weak charge-transfer contact pair¹ or complex² between oxygen and both tetrakis(dimethylamino)ethylene (TMAE) and *n*-decane. This type of complex has been observed by absorption spectrometry for several hydrocarbons which have been shown to form 1:1 pairs.³⁻⁵ TMAE has been shown to form stable complexes with a number of electron acceptors.⁶ It can also be oxidized to form both a cation radical and a dication.⁷

Since our chemiluminescent studies involve *n*-decane solutions of TMAE and oxygen we have studied the solubilities and interaction species of oxygen with both molecules. The ΔH values found appear to be the first reported for such species.

Experimental Section

Oxygen Uptake Apparatus. The pressure drop was used to measure oxygen uptake in a 10-ml. erlen-

meyer flask. In operation the liquid was degassed by freezing and pumping. Oxygen was let into the flask with the stirrer off, initial pressure zeroed quickly, and the stirrer started. With the stirrer off, the solution rate was very slow so little error arose from the initial short delay. The final pressure, pressure change, and known volume gave the amount dissolved. The pressure change was measured with a Pace transducer and a recorder. The oxygen was in 1-l. flasks in an air bath, and the sample was immersed in a stirred bath slightly above the liquid level.

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- (1) R. S. Mulliken, *J. chim. phys.*, **61**, 20 (1934).
 - (2) S. Carter, J. N. Murrell, and E. J. Rasch, *J. Chem. Soc.*, 2048 (1965).
 - (3) D. F. Evans, *ibid.*, 345 (1953).
 - (4) A. U. Mueck and J. F. Scott, *Nature*, **177**, 578 (1958).
 - (5) D. F. Evans, *J. Chem. Soc.*, 1987 (1961).
 - (6) N. Wiberg and J. W. Buckler, *Chem. Ber.*, **97**, 618 (1964).
 - (7) N. Kuwata and D. H. Geske, *J. Am. Chem. Soc.*, **86**, 2101 (1964).

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Spectrophotometric Study. The apparatus consists of two constant temperature liquid reservoirs connected by vacuum-jacketed tubing and includes spectrophotometric flow cells. The gas system above the reservoirs is used to produce a reciprocating flow of the liquid between the reservoirs or to bubble gas through the liquid phase.

A Beckman DK-2 spectrophotometer is used to monitor the absorbance of the liquid in the cells which can be placed in series or filled separately. Temperature control in the sample cell is $\pm 0.2^\circ$ during flow. Absorbances as low as 0.001 can be measured.

Material. The *n*-decane was stirred overnight with 30% fuming sulfuric acid and washed with concentrated sulfuric acid, water, and a dilute sodium hydroxide solution. After drying over activated alumina, the *n*-decane was distilled from sodium under an atmosphere of 700 torr of purified argon.

TMAE was obtained from E. I. du Pont de Nemours and Co., Wilmington, Del. It was purified by filtering through a bed of Al_2O_3 (Alcoa F-1, 4-8 mesh). This gave a material which was pure by a gas chromatographic analysis. The purified TMAE was stored under nitrogen or argon. The uncorrected melting point was -4° .

Water and similar compounds increase the irreversible reaction of TMAE with oxygen.^{7,8} All apparatus and operations were handled so as to minimize impurities including air. However, after long storage TMAE would often show a precipitate of tetramethyloxamide. Therefore, it was repurified about once a month.

During runs on the solubility there was always a slow irreversible reaction as indicated by the production of light. In the spectral runs tetramethyloxamide eventually precipitated and halted the work. The base line was determined after each run with oxygen for the work with both TMAE and decane. The rate of the irreversible reaction increased with temperature and limited studies with TMAE to 30° and lower.

The problems mentioned limited the reproducibility of data to that shown in the next section.

Results

Solubility. Table I shows the results obtained for oxygen solubility in *n*-decane and TMAE. The results reported here can be compared with a value of 0.0127 for oxygen in *n*-heptane at 25° .⁹ The solubility was taken at a series of pressures from 100 to 700 torr. It obeyed Henry's law for both *n*-decane and TMAE so best straight lines were drawn for each temperature. For these the slope, *k*, was obtained.

Table I: Solubility of Oxygen^a

<i>T</i> , °C.	<i>k</i> for <i>n</i> -decane, mmole l. ⁻¹ torr ⁻¹	<i>k</i> for TMAE, mmole l. ⁻¹ torr ⁻¹
0	0.0154	0.0151
24	0.0137	0.013 \pm 0.001
ΔH	-0.8 kcal.	-0.8 kcal.

^a $S = kP_{\text{O}_2}$ mmole/l.

There was a problem in measuring the solubilities in TMAE at room temperature (24°). Figure 1 shows a typical pressure trace. Instead of a pressure plateau, we obtained a slope due to the irreversible reaction of O_2 with TMAE. We measured the pressure drop at two points which should give minimum and maximum solubility possibilities. The *k* at 24° represents a best line drawn through the values of the mean.

A few runs were made at 0° with 10^{-3} M 1-octanol in the TMAE to learn whether this affected the solubility. These runs looked like those at 24° with "pure" TMAE, and we took maximum and minimum values which naturally include larger errors. The mean values showed no significant difference from those taken without 1-octanol.

In all the runs with TMAE the brown coloration appeared and deepened as the O_2 dissolved. There was no perceptible lag. If the stirrer was turned off and O_2 pumped away, the brown remained for several

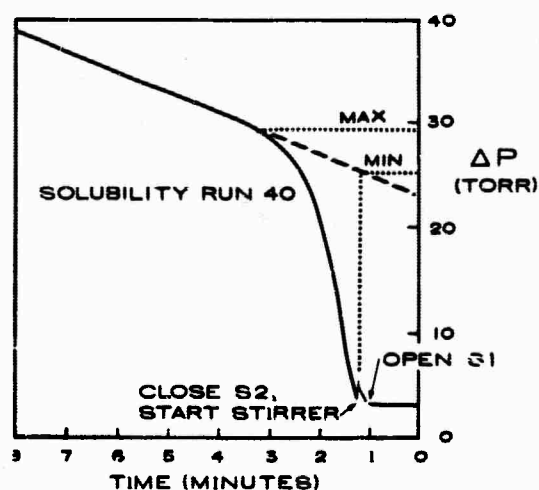


Figure 1. Solubility of O_2 in TMAE at 24° . Speedomax record showing method of obtaining maximum and minimum values of solubility.

(8) H. E. Winberg, J. R. Downing, and D. D. Coffinan, *J. Am. Chem. Soc.*, **87**, 2054 (1965).

(9) J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962.

minutes; if the stirrer was on, the brown disappeared rapidly.

Spectra. In Figures 2 and 3 we show spectra of the type used in our measurements. The solvent in all cases is *n*-decane.

Figure 2 shows in curve B the shoulder which is used to measure the *n*-decane-oxygen interaction species. Curve C shows the absorption of TMAE in *n*-decane. We find a peak at 221 $m\mu$ as opposed to 240 $m\mu$ reported elsewhere.⁸

Figure 3 shows similar curves for TMAE-oxygen systems. Curve A indicates the shoulder of the TMAE

absorption. The base line B is obtained with the spectrophotometer slits less than fully open so that curves C and D are not artifacts although less resolution is obtained below 400 $m\mu$.

Curve D is due to the difference in the molar absorptivity of TMAE and the interaction species. The absorbance of the interaction species results in the brown coloration which follows the addition or removal of oxygen with no perceptible lag.

The monocation, TMAE⁺, absorption can be seen in curve C as a narrow negative peak. The monocation is formed by the reaction⁷: $\text{TMAE}^{2+} + \text{TMAE} = 2\text{TMAE}^+$. The equilibrium is shifted to form more monocation at higher temperatures. Once again, the spectrum is due to a difference between molar absorptivities. The peak at 405 $m\mu$ is shifted from that found in acetonitrile at 385 $m\mu$.⁷

Spectrophotometric Results. The *n*-decane plus oxygen interaction was measured at 220, 225, and 230 $m\mu$. The absorbance change from oxygen-free *n*-decane was taken as the absorbance of the complex. The equilibrium quotient is first order in oxygen pressure. The *n*-decane concentration was not varied, but Evans' work³ has shown that these interactions are first order in hydrocarbon. Table II shows how the quotient changed with temperature and the calculated ΔH . The variation with wave length is probably due to a change of the extinction coefficient due to a bathochromic shift of the whole band.¹⁰

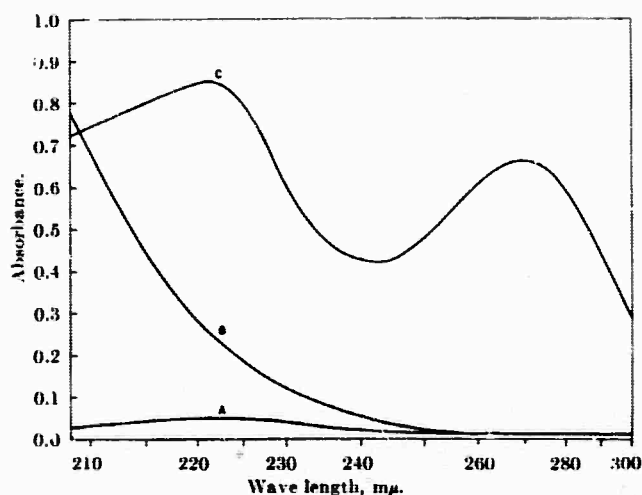


Figure 2. (A) Base line: *n*-decane vs. *n*-decane; (B) *n*-decane + 400 torr of O₂ vs. *n*-decane; (C) [TMAE], $0.65 \times 10^{-4} M$, vs. *n*-decane. All at 30°.

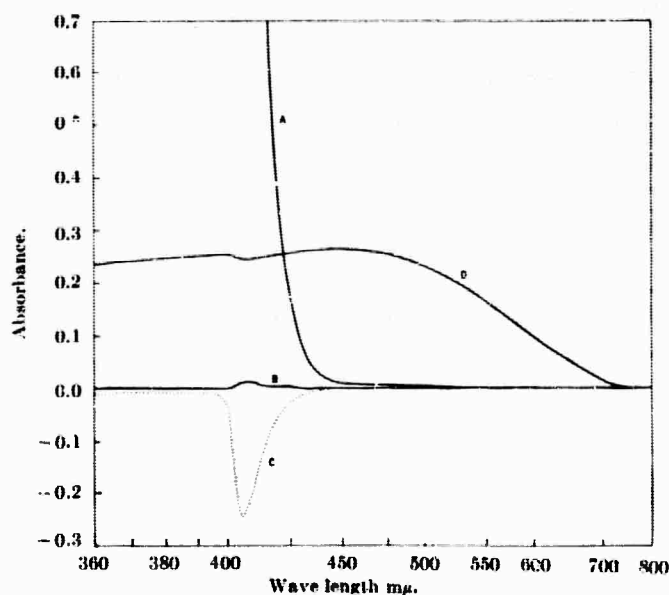


Figure 3. (A) [TMAE], 0.4 *M*, vs. *n*-decane, both 30°; (B) base line: [TMAE], 0.4 *M*, vs. [TMAE], 0.4 *M*, both 30°; (C) [TMAE], 0.4 *M*, 20°, vs. [TMAE], 0.4 *M*, 30°; (D) [TMAE], 0.4 *M*, + 1400 torr of O₂ vs. [TMAE], 0.4 *M*, both 30°.

Table II: Variation of pQ with Temperature for *n*-Decane^a

T, °C.	220 $m\mu$	225 $m\mu$	230 $m\mu$
0	3.840	4.076	4.312
10	3.861	4.092	4.323
20	3.866	4.106	4.334
30	3.886	4.115	4.344
40	3.894	4.123	4.350
50	3.898	4.125	4.346
60	3.923	4.134	4.355
ΔH	-0.52 kcal.	-0.39 kcal.	-0.29 kcal.

$$^a \text{pQ} = -\log \frac{\text{absorbance}}{[\text{n-decane}]P_{\text{O}_2}}$$

TMAE plus oxygen interaction was measured only at 450 $m\mu$ and again by subtracting the decane and any slight TMAE absorbance. In this work the TMAE

(10) H. H. Willard, L. L. Merritt, Jr., and J. A. Dean, "Instrumental Methods of Analysis," 3rd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1958, p. 7.

concentration was varied with *n*-decane as the solvent. Table III shows that the interaction is first order in both species.

Table III: Negative Log [Equilibrium Quotient] at 0° for TMAE^a

[TMAE], M	P _{O₂} , torr	Absorbance at 450 mμ	pQ
0.0219	1200	0.0123	3.329
0.0865	1200	0.051	3.313
0.128	100	0.0056	3.356
0.128	300	0.0146	3.421
0.128	500	0.0301	3.328
0.128	700	0.0410	3.338
0.128	900	0.0540	3.329
0.128	1100	0.0675	3.320
0.128	1300	0.0804	3.317
0.210	1200	0.112	3.353
0.401	1200	0.230	3.320

3.339 ± 0.006

$$^a \text{pQ} = -\log \frac{\text{absorbance}}{[\text{TMAE}]P_{\text{O}_2}}$$

Table IV shows the change of the quotient with temperature and the calculated ΔH with estimated σ .¹¹

Table IV: Variation of Average Equilibrium Quotient with Temperature for TMAE

T, °C.	pQ
0	3.34
5	3.38
10	3.35
15	3.38
20	3.42
25	3.43
30	3.43

$$-\Delta H = 1.2 \pm 0.2 \text{ kcal. mole}^{-1}$$

We attempted to measure the actual concentration of the complex by measuring the decrease in TMAE absorbance as the complex formed. No decrease could be seen, as might be expected if not much complex is formed and its spectra is similar to TMAE in the ultraviolet region. The other method for measuring the actual amount of the complex involves monitoring the free oxygen *vs.* complexed oxygen. Experimental methods all measure total, not free, oxygen by equilibrium with a second phase. The Benesi-Hildebrand equations¹² or a modification² is not applicable to our present data. A technique for adding a

known constant amount of gas would have to be developed to use these equations. Also, an inert solvent would have to be found since hydrocarbons form complexes with O₂.

Thus, we cannot calculate a concentration equilibrium constant nor the free energy of complex formation. Since O₂ and argon show similar solubilities in hydrocarbons,⁹ the amount of complexing of O₂ must be small. The similarity of O₂ solubility in *n*-decane and TMAE indicates a similar weak complex for the latter.

Discussion

From a kinetic point of view one wants to know whether the spectrally observed species can be considered a real intermediate; that is, does it have a lifetime longer than a normal collision? The contact pair formulation¹ visualizes only short lifetimes with no potential well. The experimental basis of this has been questioned,² and it appears possible that even weak interactions indicate that a complex is formed. That is to say, there will be no extinction coefficient unless there is a real complex in a potential well with an equilibrium constant and a lifetime long compared with collision time. Under these circumstances, the complex can be considered an intermediate for subsequent reactions, which is of importance in the consideration of third-order reactions. These need not be termolecular, but rather the result of a 1:1 complex reacting with a third molecule.

In alkane oxidation Denisov¹³ has measured initiation kinetics which are first order in oxygen and second order in alkane. This could be due to a reaction between the alkane-oxygen complex and an alkane molecule to form free radicals.

The evidence from our measurements is that there is a slight negative enthalpy for both interaction species. For TMAE-O₂ it amounts to a few hundred calories even if we subtract the enthalpy of solution of oxygen from the measured enthalpy of formation of the peak at 450 mμ. Although the negative enthalpy does not prove there is a free energy well, it makes it appear more probable.

If the complex is an intermediate and the equilibrium is rapid compared to subsequent reactions, the ΔH will enter the observed activation energy.

The effect of traces of water³ in increasing the irreversible oxidation of TMAE can be understood in terms of the donor-acceptor theories of Mulliken,¹

(11) A. M. Mood, "Introduction to the Theory of Statistics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 291.

(12) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

(13) E. E. Denisov, *Kinetika i Kataliz*, **4**, 53 (1963).

who points out that the change from a weak complex to an ion pair is assisted by a polar environment or by formation of a complex ion. Thus, water could be expected to react with the TMAE-O₂ complex to give ion pairs. This irreversible reaction will be the subject of the next paper in this series.

Acknowledgment. The reversible brown coloration due to the TMAE-O₂ interaction species was first

noted by Charles M. Drew of this laboratory. Discussions with Drs. R. H. Knipe, P. Hammond, and W. Urry have been very helpful. Results by H. E. Winberg, J. R. Downing, D. D. Coffman, and J. P. Paris of Du Pont on TMAE were made available to us before their publication. This research was supported in part by the Advanced Research Projects Agency, Chemistry Office, Order No. 205-62-AM5.

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KEY WORDS

Tetrakis(dimethylamino)ethylene, *n*-decane,
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